The Dielectric Polarization of Liquids

I Halogenated Hydrocarbons
II Fatty Acids

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Princeton

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I Halogenated Hydrocarbons
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A DISSERTATION

PRESENTED TO THE

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HORACE ELTON ROGERS

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THE DIELECTRIC POLARIZATION OF LIQUIDS. I. THE ELECTRIC MOMENTS OF THE ALKYL HALIDES AND HALOGENATED METHANES

The electric moments of butyl chloride, bromide and iodide and heptyl bromide have been determined with a view to ascertaining the effect of the length of the hydrocarbon chain upon the moment of the molecule and to observing whether the variation from chloride to bromide to iodide is the same in large molecules as in small. At the same time it is possible to study the dependence of the mutual orienting effects of the molecules upon molecular size. The previously unmeasured bromine and iodine substituted methanes have been investigated in order to throw further light upon the mutual repulsion of atoms or groups in the same molecule.

Method of Measurement

The methods of measurement and calculation used in the present work have been described in the first two papers of the series[1] on dielectric polarization, and a subsequently developed cell with four different fixed capacities, which was used in some of the measurements, has been described in a later paper. The dielectric constants[2] were measured with the capacity bridge originally used, a frequency of 5×10^5 cycles, corresponding to a wave length of 600 meters, being employed as before. The errors were similar to those described in the last mentioned paper, dielectric constant values below 5 having a probable error of 0.2% and those above 5 having a probable error of 0.5%. The relative error within a given series of measurements was much smaller in both cases. Since the same type of pycnometer was used as in the earlier work, the probable error in the densities was the same, being about 0.07% in the low temperature determinations and not more than 0.03% in the measurements above 0°.

Preparation of Materials

Heptane.—Pure normal heptane was obtained from the Ethyl Gasoline Corporation. As the boiling point, refractive index, and dielectric constant of a sample were not appreciably different after washing with sulfuric acid, followed by sodium carbonate solution and water, drying over calcium chloride and finally distilling over sodium, the heptane was used without purification.

Benzene.—Merck's C. P. benzene was washed three times with concentrated sulfuric acid, followed by dilute sodium hydroxide solution and water, dried over calcium chloride and crystallized twice; m. p. 5.47°. It was then allowed to stand over sodium and distilled from it; b. p. 80.1°; n_D^{20} 1.50135.

[1] Smyth, Morgan and Boyce, *J. Am. Chem. Soc.*, **50**, 1536 (1928); Smyth and Morgan, *ibid.*, **50**, 1547 (1928).

[2] Smyth and Stoops, *ibid.*, **51**, 3312 (1929).

Butyl Chloride.—*n*-Butyl chloride obtained from the Eastman Kodak Company was refluxed gently with concentrated sulfuric acid, distilled, washed with water, dried over calcium chloride and distilled; b. p. 77.5°; n_D^{20} 1.40148.

Butyl Bromide.—*n*-Butyl bromide obtained from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, then with sodium carbonate solution, dried over calcium chloride and distilled; b. p. 101.0°; n_D^{20} 1.43985.

Butyl Iodide.—*n*-Butyl iodide obtained from the Eastman Kodak Company was shaken once with ice-cold concentrated sulfuric acid and eight times with dilute sodium hydroxide, washed with water, dried over calcium chloride and distilled at reduced pressure; d_4^{20} 1.616.

Heptyl Bromide.—*n*-Heptyl bromide obtained from the Eastman Kodak Company was washed with cold concentrated sulfuric acid, sodium carbonate solution, and water, dried over calcium chloride and distilled at reduced pressure. A fraction boiling within a 0.2° interval was taken; d_4^{16} 1.144; n_D^{20} 1.44972. "International Critical Tables" give d_4^{16} 1.133, in good agreement with the value d_4^{16} 1.134 obtained for the unpurified material. The purified material was treated again in the same way and the product obtained had the same density as before, d_4^{16} 1.144. This was, therefore, concluded to be the correct value for the pure material.

Methylene Bromide.—Material obtained from the Eastman Kodak Company was washed with dilute sodium carbonate solution and water, dried over calcium chloride and distilled at reduced pressure; d_4^{20} 2.4921; n_D^{20} 1.53559.

Methylene Iodide.—Kahlbaum's methylene iodide was washed with dilute sodium hydroxide solution and water, dried over calcium chloride and distilled at reduced pressure; d_4^{25} 3.3104.

Bromoform.—Material obtained from the Eastman Kodak Company was washed with concentrated sulfuric acid, followed by dilute sodium hydroxide solution and water, dried over anhydrous potassium carbonate and distilled at reduced pressure; d_4^{20} 2.889.

Iodoform.—Kahlbaum's iodoform, which melted at 119.0°, was used without purification.

Experimental Results

The densities, which showed but slight departure from a linear dependence upon temperature, were determined at approximately 25° intervals and the dielectric constants at 15° intervals. The majority of the densities, d, and dielectric constants, ϵ, in Table I were obtained at 10° intervals by graphical interpolation, and the polarizations, P_2, of the polar components were calculated from them by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{c_1 M_1 + c_2 M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the individual components. The solutions of methylene bromide, methylene iodide and bromoform were measured at the same two or three fixed temperatures and, therefore, require no interpolation to make them comparable.

Discussion of Results

When the P_2–c_2 curves are extrapolated to $c_2 = 0$, the values of P obtained, designated as P_∞, give a straight line when multiplied by T and

Table I

Dielectric Constants and Densities of Solutions and Polarizations of Polar Components

Heptane–Butyl Chloride

Mole fr. of C_4H_9Cl =	0	0.0242	0.0653	0.0889	0.1562	0.2191	0.2617	0.5619	0.8623	1.000
t, °C.	ϵ									
−90	2.083	2.219	2.440	2.567	2.954	3.359	3.659	6.302	10.16	12.24
−70	2.055	2.175	2.376	2.485	2.837	3.184	3.453	5.792	9.228	10.98
−50	2.027	2.135	2.315	2.413	2.732	3.038	3.266	5.322	8.465	9.940
−30	1.999	2.096	2.259	2.347	2.635	2.904	3.122	4.924	7.743	9.073
−10	1.972	2.058	2.206	2.285	2.547	2.792	2.986	4.586	7.077	8.320
10	1.944	2.022	2.157	2.227	2.466	2.688	2.861	4.285	6.518	7.663
30	1.916	1.985	2.108	2.174	2.393	2.591	2.745	4.025	6.062	7.090
50	1.888	1.950	2.059	2.122	2.319	2.494	2.642	3.792	5.676	6.558
70	1.858	1.913	2.007	2.070	2.248	2.410	2.543	3.570	5.250	6.045
	d									
−90	0.7752	0.7778	0.7836	0.7864	0.7993	0.8025	0.8205	0.8820	0.9618	1.0050
−70	.7587	.7613	.7678	.7700	.7826	.7872	.8029	.8630	.9400	.9794
−50	.7420	.7448	.7513	.7539	.7659	.7718	.7853	.8438	.9191	.9580
−30	.7252	.7280	.7347	.7375	.7488	.7561	.7673	.8247	.8980	.9375
−10	.7088	.7114	.7181	.7209	.7317	.7402	.7490	.8057	.8769	.9157
10	.6921	.6947	.7011	.7043	.7148	.7243	.7313	.7867	.8559	.8950
30	.6755	.6775	.6843	.6878	.6975	.7070	.7130	.7675	.8355	.8736
50	.6576	.6606	.6668	.6708	.6790	.6889	.6949	.7475	.8148	.8513
70	.6392	.6428	.6486	.6528	.6603	.6708	.6759	.7271	.7925	.8275
	$P_2(C_4H_9Cl)$									
−90	157.7	153.2	141.2	137.1	127.5	124.5	118.1	96.76	79.52	72.68
−70	146.5	143.6	133.7	129.4	122.0	118.1	113.3	94.82	79.12	70.98
−50	136.5	134.6	126.3	122.5	116.8	112.7	108.4	92.50	78.72	72.32
−30	128.5	126.5	120.2	116.7	112.1	107.9	105.2	90.34	78.12	71.96
−10	121.7	120.7	114.6	111.3	107.9	103.9	102.0	88.30	77.33	71.67
10	116.1	115.0	110.1	106.3	103.8	101.1	98.62	86.32	76.60	71.29
30	111.3	109.6	105.4	102.4	100.8	97.73	95.64	84.57	76.02	70.96
50	106.6	101.5	99.10	97.44	97.01	94.35	92.75	82.88	75.58	70.59
70	102.4	94.48	92.42	93.45	93.61	90.02	90.13	81.04	74.70	70.12

Heptane–Butyl Bromide

Mole fr. of C_4H_9Br =	0.0456	0.0930	0.1409	0.2579	0.4154	0.5959	0.8413	1.000
t, °C.	ϵ							
−90	2.349	2.588	2.854	3.548	4.687	6.280	8.970	11.08
−70	2.289	2.513	2.751	3.379	4.389	5.810	8.220	10.14
−50	2.239	2.441	2.653	3.226	4.119	5.405	7.565	9.258
−30	2.193	2.373	2.568	3.086	3.886	5.044	6.984	8.520
−10	2.149	2.310	2.491	2.957	3.679	4.732	6.474	7.880
10	2.107	2.251	2.417	2.843	3.499	4.454	6.039	7.315
30	2.064	2.197	2.346	2.737	3.336	4.203	5.640	6.799
50	2.022	2.146	2.279	2.640	3.187	3.966	5.290	6.345
70	1.979	2.097	2.217	2.547	3.050	3.761	4.969	5.930
90	1.938	2.049	2.158	2.455	2.914	3.577	4.662	5.535

TABLE I (*Continued*)

Mole fr. of C_4H_9Br =	0.0456	0.0930	0.1409	0.2579	0.4154	0.5959	0.8413	1.000
t, °C.				d				
−90	0.7960	0.8195	0.8432	0.9072	0.9986	1.1152	1.2967	1.4310
−70	.7783	.8022	.8260	.8884	.9781	1.0927	1.2708	1.4040
−50	.7616	.7849	.8087	.8694	.9575	1.0698	1.2449	1.3735
−30	.7456	.7679	.7913	.8505	.9372	1.0472	1.2188	1.3450
−10	.7295	.7510	.7740	.8318	.9170	1.0245	1.1926	1.3170
10	.7125	.7337	.7560	.8127	.8964	1.0017	1.1663	1.2880
30	.6949	.7159	.7375	.7931	.8750	.9780	1.1397	1.2592
50	.6775	.6977	.7183	.7723	.8528	.9542	1.1129	1.2300
70	.6589	.6786	.6993	.7514	.8307	.9298	1.0853	1.2005
90	.6397	.6590	.6803	.7306	.8073	.9043	1.0562	1.1695

	P_∞	$P_2(C_4H_9Br)$							
−90	157.8	153.2	136.3	129.7	118.6	105.2	94.2	80.9	73.8
−70	146.5	144.4	130.9	124.2	114.7	102.4	92.2	80.2	73.5
−50	138.6	136.2	124.7	118.5	111.0	99.53	90.6	79.4	73.2
−30	131.7	129.7	118.9	113.9	107.5	96.88	88.9	78.7	72.8
−10	124.2	124.1	113.4	110.6	104.0	94.35	87.0	77.9	72.4
10	118.6	119.3	109.2	106.1	100.9	92.18	86.0	77.2	72.1
30	113.4	115.1	105.7	102.1	98.02	90.28	84.7	76.5	71.7
50	109.2	109.3	101.9	98.94	95.85	88.46	83.2	75.9	71.3
70	106.2	104.5	99.57	95.81	93.56	86.77	82.0	75.2	70.9
90	103.0	102.9	98.34	93.84	91.21	85.13	81.1	74.6	70.5

Heptane–Butyl Iodide

Mole fr. of C_4H_9I =	0.0386	0.0831	0.1698	0.2943	0.5462	0.8090	1.000
t, °C.				ϵ			
−80	2.247	2.450	2.862	3.529	5.044	7.085	8.890
−60	2.201	2.386	2.760	3.351	4.729	6.543	8.180
−40	2.157	2.325	2.668	3.195	4.445	6.082	7.534
−20	2.115	2.271	2.585	3.063	4.188	5.673	7.002
0	2.076	2.219	2.506	2.939	3.971	5.304	6.542
20	2.038	2.169	2.432	2.820	3.783	5.005	6.117
40	2.001	2.119	2.360	2.718	3.614	4.755	5.737
60	1.964	2.073	2.295	2.630	3.465	4.507	5.421
80	1.925	2.027	2.229	2.556	3.318	4.254	5.108

	d						
−80	0.7993	0.8352	0.9082	1.0221	1.2619	1.5497	1.7842
−60	.7818	.8172	.8892	.9993	1.2361	1.5187	1.7505
−40	.7644	.7992	.8702	.9771	1.2109	1.4883	1.7168
−20	.7470	.7810	.8509	.9549	1.1854	1.4582	1.6832
0	.7296	.7628	.8314	.9329	1.1596	1.4278	1.6495
20	.7118	.7446	.8112	.9111	1.1339	1.3976	1.6158
40	.6940	.7263	.7912	.8900	1.1079	1.3674	1.5824
60	.6757	.7075	.7711	.8675	1.0816	1.3369	1.5485
80	.6571	.6885	.7505	.8449	1.0551	1.3063	1.5144

TABLE I (*Continued*)

t, °C.	Mole fr. of C_4H_9I = P_∞	0.0386	0.0831	0.1698	0.2943	0.5462	0.8090	1.000
					$P_2(C_4H_9I)$			
−80	136.6	137.6	124.6	116.4	107.6	93.1	81.7	74.6
−60	127.1	123.0	119.0	111.9	104.0	91.2	80.6	74.1
−40	120.9	116.3	114.0	108.2	100.8	89.1	79.6	73.5
−20	115.4	111.2	110.1	104.8	98.2	87.4	78.6	72.9
0	111.1	107.1	106.3	101.6	95.5	85.9	77.5	72.4
20	107.6	104.4	103.1	98.9	92.7	84.6	76.8	71.8
40	103.0	100.3	99.0	95.8	90.2	83.4	76.2	71.1
60	98.4	96.7	95.9	93.2	88.7	82.5	75.5	70.8
80	95.6	92.9	93.1	90.5	87.9	81.4	74.5	70.2

Heptane–Heptyl Bromide

t, °C.	Mole fr. of $C_7H_{15}Br$ =	0.0488	0.0889	0.1626	0.3330	0.5327	1.000
				c			
−70		2.297	2.491	2.862	3.704	4.809	7.385
−50		2.247	2.422	2.755	3.515	4.498	6.875
−30		2.198	2.356	2.656	3.348	4.214	6.392
−10		2.152	2.294	2.567	3.200	3.969	5.957
10		2.109	2.237	2.489	3.067	3.767	5.582
30		2.067	2.184	2.417	2.950	3.595	5.255
50		2.024	2.133	2.349	2.840	3.437	4.970
70		1.980	2.083	2.278	2.734	3.284	4.711
90		1.936	2.033	2.210	2.632	3.134	4.476
				d			
−70		0.7831	0.8039	0.8428	0.9348	1.0243	1.2370
−50		.7667	.7871	.8249	.9166	1.0044	1.2160
−30		.7502	.7702	.8075	.8981	.9849	1.1944
−10		.7333	.7533	.7895	.8793	.9657	1.1725
10		.7165	.7359	.7712	.8606	.9456	1.1507
30		.6988	.7184	.7534	.8420	.9255	1.1285
50		.6810	.7004	.7354	.8227	.9056	1.1065
70		.6632	.6821	.7171	.8032	.8858	1.0847
90		.6442	.6633	.6978	.7836	.8648	1.0622
	P_∞				$P_2(C_7H_{15}Br)$		
−70	...	152.3	146.1	139.0	123.8	115.7	98.5
−50	149.6	145.3	139.7	133.6	119.9	112.8	97.5
−30	141.6	138.4	133.7	128.4	116.5	109.9	96.3
−10	134.6	132.7	128.0	124.0	113.4	107.1	95.1
10	128.3	127.7	123.3	120.5	110.6	105.0	94.0
30	125.5	124.4	119.6	117.3	108.2	103.4	93.0
50	...	118.2	115.2	113.9	105.7	101.6	92.1
70	...	112.1	111.6	109.9	103.3	99.7	91.3
90	...	108.4	108.8	106.9	101.0	97.0	90.5

Benzene–Methylene Bromide

t, °C.	Mole fr. of CH_2Br_2 =	0.0496	0.0947	0.2038	0.5618	0.8114	1.000
				e			
10		2.460	2.596	2.957	4.420	5.884	7.772
40		2.383	2.502	2.815	4.088	5.335	6.678
70		2.293	2.401	2.676	3.841	4.848	

TABLE I (*Continued*)

t, °C.	Mole fr. of CH_2Br_2 =	0.0496	0.0947	0.2038	0.5618	0.8114	1.000
				d			
10		0.9530	1.0117	1.1607	1.7015	2.1418	2.5438
40		.9192	.9759	1.1202	1.6463	2.0734	2.4442
70		.8844	.9395	1.0795	1.5984	2.0042	
	P_∞			$P_2(CH_2Br_2)$			
10	64.4	62.4	60.8	58.6	52.7	49.3	47.1
40	62.1	60.1	58.5	56.5	51.4	48.5	46.5
70	59.0	56.9	56.5	54.7	50.6	47.6	

Benzene–Methylene Iodide

t, °C.	Mole fr. of CH_2I_2 =	0.0268	0.0449	0.0636	0.1337	0.1943	1.000
				ϵ			
25		2.341	2.384	2.425	2.592	2.734	5.316
50		2.282	2.322	2.359	2.524	2.646	
				d			
25		0.9330	0.9721	1.0137	1.1728	1.3065	3.3105
50		.9045	.9432	0.9832	1.1351	1.2706	
	P_∞			$P_2(CH_2I_2)$			
25	56.3	54.4	56.2	55.7	55.1	56.1	47.74
50	54.6	52.2	54.2	54.2	55.6	53.0	

Benzene–Bromoform

t, °C.	Mole fr. of $CHBr_3$ =	0.0409	0.0573	0.0718	0.0929	0.2340	0.5047	0.7358	1.000
					ϵ				
10		2.308	2.411	2.438	2.477	2.726	3.232	3.726	4.404
40		2.315	2.340	2.365	2.399	2.623	3.075	3.506	4.084
70		2.234	2.258	2.284	2.313	2.522	2.924	3.315	3.816
					d				
10		0.9711	1.0045	1.0330	1.0751	1.3591	1.9068	2.3818	2.9189
40		.9366	.9689	.9969	1.0380	1.3144	1.8487	2.3134	2.8383
70		.8997	.9333	.9603	1.0004	1.2692	1.7898	2.2446	2.7597
	P_∞				$P_2(CHBr_3)$				
10	51.0	48.5	50.8	50.1	50.4	49.1	47.5	46.6	46.05
40	49.9	48.6	49.1	49.2	49.1	48.0	46.6	45.6	45.17
70	48.5	45.0	47.3	46.8	46.8	46.9	45.6	44.9	44.37

Benzene–Iodoform

Mole fr. of CHI_3 = t, °C.	0	0.0063	0.0222	0.0352	0	0.0063	0.0222	0.0352
		ϵ						
10	2.315	2.323	2.361	2.387	0.8896	0.9096	0.9663	1.0100
20	2.295	2.307	2.341	2.366	.8786	.8991	.9550	.9989
30	2.274	2.291	2.321	2.345	.8682	.8880	.9436	.9869
40	2.253	2.272	2.298	2.322	.8574	.8768	.9322	.9750
50	2.232	2.252	2.275	2.299	.8466	.8657	.9210	.9631
60	2.210	2.230	2.250	2.274	.8357	.8546	.9096	.9512
70	2.188	2.206	2.226	2.248	.8246	.8434	.8979	.9392

TABLE I (*Concluded*)

t, °C.	Mole fr. of CHI_3 = P_∞	0.0063	0.0222	0.0352
		$P_2(CHI_3)$		
10	...	56.5	59.6	53.5
20	61.5	63.6	60.1	59.5
30	...	66.8	61.0	60.1
40	...	73.2	60.1	59.5
50	59.6	87.6	58.8	59.0
60	...	87.6	57.0	58.1
70	...	84.4	55.7	56.4

plotted against T (Fig. 1), as required by the Debye equation: $P = a + b/T$, in which $a = P_E + P_A$, the sum of the electronic polarization, P_E, and the atomic, P_A, and $b = 4\pi N\mu^2/9k$, N being the Avogadro number, 6.061×10^{23}, μ, the electric moment, and k, the molecular gas constant, 1.372×10^{-16}. When the equation is written in the form $(P_\infty - a)\ T = b$, it is evident that it can be tested by the constancy of $(P_\infty - a)T$, the values of which are given in Table II.

TABLE II

VALUES OF $(P_\infty - a)T$

T, °A.	$(P_\infty - a)T$			
	C_4H_9Cl	C_4H_9Br	C_4H_9I	$C_7H_{15}Br$
183	21810	20290	...	...
193	21920	20270	15900	...
203	21920	20220	16180	...
213	21940	20380	15530	20510
223	21850	20450	15500	20590
233	21800	20130	15540	20780
243	21870	20610	15650	20630
253	21960	20420	15480	20440
263	21880	20330	15520	20490
273	22170	20280	15530	20310
283	21960	20280	15730	20260
293	21920	20330	15650	20690
303	22060	20150	15630	20850
313	21910	20410	15270	20630
323	22000	20120	14660	...
333	21910	20280	15060	...
343	21920	20340	14750	...
353	...	20400	14620	...

In the case of butyl iodide, a small decrease in the values of $(P_\infty - a)T$ accompanies rising temperature at the higher temperatures, probably because of slight decomposition of the substance. Below 30° for the butyl iodide and over the entire temperature range within which the other substances are liquid, the values of $(P_\infty - a)T$ are constant, giving further proof, if further proof is needed, of the applicability of the Debye equation to polar liquids highly diluted by non-polar.

The best values of a and b were obtained from the curves in Fig. 1 and the electric moments were then calculated from b. The values of P_E at infinite wave length were calculated from the molar refractions given in Landolt–Börnstein (5th ed.) by means of the equation, $P_E = [1 - \lambda_0^2/\lambda^2][(n^2 - 1)M/(n^2 + 2)d]$, in which n is the refractive index for light of wave length λ, λ_0 is the wave length corresponding to a characteristic vibration frequency in the ultraviolet region, and d is the density. As dispersion data were not available for heptyl bromide, the value of P_E at infinite wave length was estimated by subtracting 1.0, a difference analogous to those found for the other halides, from 42.20, the molar refraction for the sodium D-line. The result, 41.2, should be within 0.3 of the correct value. The atomic polarization, P_A, has been obtained by subtracting P_E from a. The results are shown in Table III.

Fig. 1.—Variation of $P_\infty T$ with T.

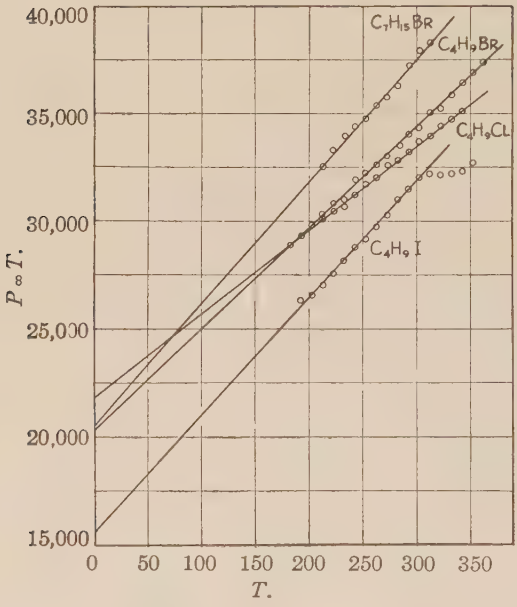

TABLE III

VALUES OF FUNDAMENTAL CONSTANTS

	a	P_E	P_A	b	$\mu \times 10^{18}$
C_4H_9Cl	38.5	24.9	13.6	21920	1.88
C_4H_9Br	46.9	27.6	19.3	20300	1.81
C_4H_9I	54.2	32.3	21.9	15530	1.59
$C_7H_{15}Br$	56.7	41.2	15.5	20610	1.83

The values of P_A are surprisingly high and may be considerably in error, as a small change in the curve has a large effect upon a and, consequently, an even greater effect upon the difference, $a - P_E$, but the accuracy of the curves is such as to render a small P_A for these substances highly improbable. Moreover, a value of 12.3 has been determined with some accuracy for ethyl iodide[2] and a rough value of 11 has been found for ethyl bromide.[1] Preliminary measurements carried out in this Laboratory upon heptyl bromide in the solid state indicate a value for P_A of the same order of magnitude as that here found. In the butyl halides, the values increase

from chloride to bromide to iodide, but, in view of the uncertainty of the values, great significance cannot be attached to this.

The substituted methanes were measured over too limited a range of temperature to permit of an accurate determination of a and b by plotting P_∞ against $1/T$. As is very commonly done, a was assumed equal to MR_D, the molar refraction for the D-sodium line, and the electric moment was calculated from $P_\infty - MR_D$. The values of MR_D for methylene bromide and bromoform were taken directly from Landolt–Börnstein (5th ed.), while those for methylene iodide and iodoform were calculated as the sum of the atomic refractions, the accuracy of the values thus obtained being quite sufficient for the purpose. Values of the electric moments calculated at different temperatures showed very close agreement except in the case of iodoform, the results for which are less accurate than the others because of its low solubility and decomposition in solution. The small values of the difference $P_\infty - MR_D$ for this substance increase the relative error of the moment. At 20° the value obtained was 0.84×10^{-18}, and at 70°, 0.77×10^{-18}. The necessary neglect of P_A in calculating this moment causes the mean value 0.8×10^{-18} given in Table IV to be too high. Indeed, if iodoform had a value of P_A comparable to those given in Table III, its moment would be zero. It seems probable that the true value of the moment of iodoform is little more than half the value given in Table IV, while the values for methylene bromide and iodide and bromoform are also a little high because of neglect of P_A, which, however, affects these moments less than that of iodoform because of their higher values. As most investigators have neglected P_A[3] in calculating the moment, it seems best, for the sake of comparison, to use these values, bearing in mind the fact that they are a little high, rather than to subtract fictitious values of P_A of reasonable size, which might be expected to give more nearly correct values for the moments. The good agreement of the values at different temperatures, except in the case of iodoform, indicates that they are not far from the true values. The significance of the results shown in Table IV, together with the moments of other similar molecules, will be discussed presently.

Earlier papers have discussed the variation of the polarization with concentration as evidence of the mutual effects of the polar molecules in producing orientation or association.[4] It has been shown that the orienting effect of the molecules of a liquid upon one another depends not only on the size of their electric doublets, but also upon the location of the doublet or doublets in the molecule and upon the geometrical shape of the molecule. It is interesting to compare these effects in the closely related molecules investigated in the present work.

[3] See Smyth, *J. Am. Chem. Soc.*, **51,** 2051 (1929).

[4] See particularly Smyth and Stoops, *ibid.*, **51,** 3330 (1929); also Smyth, *Chem. Reviews*, **6,** 549 (1929).

The molecule of an alkyl halide may be regarded as containing a single electric doublet located in the neighborhood of the bond between the halogen and the carbon chain. The effect of this doublet upon neighboring molecules depends upon its moment and upon the sizes of the halogen and the hydrocarbon chain which screen its force field. The deviation of the P_{12}–c_2 curves from linearity has been used as a qualitative indication of association or orientation. The effect is so great in hexane–ethyl bromide mixtures[1] that the curve actually passes through a maximum, which flattens out with rising temperature as increased thermal agitation reduces the molecular orientation. The moment of the ethyl iodide molecule is slightly smaller than that of the bromide and the screening effect[2] of the iodine is somewhat larger than that of the bromine. Consequently, the mutual effect of the molecules is not sufficient to cause a maximum in the P_{12}–c_2 curves as in the case of ethyl bromide. When butyl chloride, bromide and iodide are compared with one another, the differences are not pronounced as the screening effect of the large butyl groups so reduces the intermolecular action that the differences between the effects of the halogens are small.

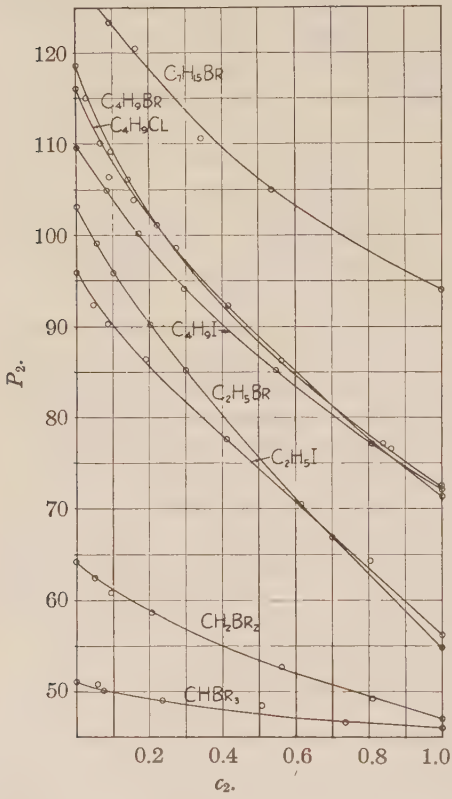

Fig. 2.—Variation of P_2 with concentration at 10°.

In comparing the P_{12}–c_2 curves for different substances, it must be borne in mind that differences in P_E affect the relative rate of change of P_2 with c_2 and hence the shape of the P_{12}–c_2 curves. Indeed, this seems to be the principal cause of the differences in these curves, for the P_2–c_2 curves in Fig. 2 show only small differences in curvature. The heptyl bromide curve has the smallest slope. The butyl halide curves have a slightly greater slope and lie close together. The ethyl bromide and ethyl iodide curves are very similar, the slope of the latter being slightly less. Differences in P_E and P_A for the different substances are responsible for the spacing of the curves.

At the bottom of the diagram lie the curves for methylene bromide and

bromoform, which, because of the small size of their moments and the screening of the doublets by the bromines, show little intermolecular action. The corresponding iodine compounds are not shown, as some of their P_2 values are in error because of decomposition.

The temperature variation of P_2 for the pure substance gives further evidence of the intermolecular action. The values of P_2 for pure ethyl bromide increase slightly with rising temperature until the boiling point is approached, instead of decreasing according to the requirements of the Debye equation, because increasing thermal agitation decreases the intermolecular action which reduces the polarization. In ethyl iodide the intermolecular action is enough smaller to permit decrease of polarization with rising temperature even at the lower temperatures where its effect is greater. In the butyl halides the decrease of P_2 with rising temperature is greater and, in heptyl bromide, still greater.

The moments calculated from the values of P_∞ are given in Table IV together with a number of values previously determined, the latter being followed by their literature references.

TABLE IV

ELECTRIC MOMENTS OF HALOGEN COMPOUNDS $\times 10^{18}$

X =	Cl	Br	I
CH_3X	1.7[a]	..	1.31[b]
C_2H_5X	2.0[a]	1.86[c]	1.66[d]
C_4H_9X	1.88	1.81	1.59
$C_7H_{15}X$	..	1.83	..
CH_2X_2	1.6[e]	1.39	1.08
CHX_3	1.05[c]	0.99	0.8
CX_4	0[e]	..	..
CH_3CHX_2	2.05[f]	..	..

[a] Sircar, *Indian J. Phys.*, **12,** 197 (1928); [b] Mahanti and Sen Gupta, *ibid.*, **12,** 181 (1928); [c] Smyth and Morgan, Ref. 1; [d] Smyth and Stoops, Ref. 2; [e] Sänger, *Physik. Z.*, **27,** 556 (1926); [f] Ghosh, Mahanti and Sen Gupta, *Z. Physik*, **54,** 711 (1929).

The influence of the length of the carbon chain upon the moment of the molecule has been discussed previously, but a quantitative treatment of the theory has been attempted in the present investigation.[5] As the result of the treatment is not conclusive, the details are not given. The moments induced throughout the molecule by the principal doublet at the end of the chain and the moments induced in turn by these induced moments are calculated from the polarizabilities of the different parts of the molecule, which are obtained from the refractions associated with the bonds.[6] The calculated increase in moment due to the direct effect of the principal doublet is very small in the third carbon of the chain and negligible thereafter, which is in agreement with the absence of any increase in the observed

[5] Smyth, *J. Am. Chem. Soc.*, **51,** 2380 (1929).

[6] *Cf.* Smyth, *Phil. Mag.*, **50,** 361 (1925).

moments with increase in the size of the alkyl group beyond ethyl. However, the secondary moments induced by those already induced by the principal doublet are calculated as continuing with decreasing size through a chain much longer than two carbons. This would cause an increase in moment with increase in the size of the alkyl group far beyond ethyl, which the agreement of the values for the ethyl and the butyl halides and, in the case of the bromides, the heptyl as well, shows to be non-existent. The rough approximations necessary in these calculations are much more apt to cause serious error in the case of the secondary moments. Indeed, they are quite sufficient to cause the not inconsiderable values calculated for these secondary moments, which the experimental results show to be negligible in the longer molecules. In view of this, it may be concluded that the results of theory and experiment are not irreconcilable, but the failure to obtain positive agreement is unsatisfactory.

The moments of the chlorinated methanes were considered at a time when very inadequate values were available.[7] It was shown that, if the tetrahedral structure of the molecule remained undistorted, the moment of methylene chloride should be 1.15 times that of methyl chloride, which should be identical with that of chloroform, while that of the symmetrical carbon tetrachloride molecule should be zero. The same relations should, of course, hold among the bromine and iodine compounds. Sänger obtained a higher value for methyl chloride than that given in Table IV, but, as Sircar's value 1.69×10^{-18} agrees well with an unpublished result obtained by Dr. S. O. Morgan, the value 1.7×10^{-18} has been adopted as correct.

The deviations of the observed values from those calculated on the basis of an undistorted tetrahedral structure may be conveniently explained by resolving the system of charges making up the methylene halide molecule into two doublets with their axes in the two imaginary lines joining the halogen nuclei to the carbon nucleus. The moment of the molecule, as a whole, is the resultant of the moments of these two doublets and is, of course, smaller the larger the angle between the axes of the doublets. The distance between a carbon nucleus and the nucleus of an attached chlorine atom is calculated to be 1.70 Å.[8] If there were no distortion of the tetrahedral structure of methylene chloride, the angle between the axes of the two doublets would be 110° and the distance between the two chlorine nuclei would, therefore, be 2.78 Å. The radius of the chlorine atom calculated by Huggins[9] from x-ray data is 0.97 Å., from which the distance between the outermost electrons in the two chlorines, a very vague quantity, would be calculated as 0.84 Å. A quantity more significant for these considerations is the atomic diameter obtained from the kinetic theory of gases, which

[7] Smyth, *Phil. Mag.*, **47,** 530 (1924).
[8] Pauling, *Z. Krist.*, **67,** 377 (1928).
[9] Huggins, *Phys. Rev.*, **28,** 1086 (1926).

might be expected to set a limit to the distance of nearest approach of the chlorine nuclei in the absence of strong forces of compression. Approximate values for this diameter may be calculated by an indirect method. The radius of the collision sphere of the argon atom determined by Rankine and Smith[10] from viscosity measurements is 1.44 Å. as compared with an atomic radius 0.93 Å. calculated by Huggins. If a proportionate difference exists for the chlorine atom, the latter has a collision sphere of radius 1.50 Å., which necessitates a distance of 3.0 Å. between the chlorine nuclei in methylene chloride if the spheres are in actual contact and uncompressed, instead of the 2.78 Å. calculated for the undistorted tetrahedral structure. A widening of the angle between the doublet axes from 110 to 124° is, therefore, required and, as a result, the moment of the molecule, as a whole, is reduced from the value calculated for the undistorted molecule, $1.15 \times 1.7 \times 10^{-18}$, to $0.94 \times 1.7 \times 10^{-18} = 1.6 \times 10^{-18}$, in agreement with the observed value. Similarly, in methylene bromide, the distance between the nuclei of the bromines and that of the carbon is given as 1.85 Å., from which the separation of the bromine nuclei may be calculated as 3.02 Å. in the absence of distortion of the tetrahedral structure. The bromine radius given by Huggins is 1.09 Å. and that of krypton is 1.06 Å., while the radius of the collision sphere of krypton found by Rankine and Smith is 1.55 Å., which figures give a radius for the sphere of repulsion of the bromine atom of 1.60 Å. The nuclear separation of the bromines in methylene bromide should, therefore, be 3.20 Å. instead of 3.02 Å., the angle between the doublets would be widened to 120°, and the resultant moment would be identical with that of methyl bromide. No accurate value for the latter is available in the literature, but an unpublished value determined by Dr. S. O. Morgan agrees within the limit of the experimental error with the moment of methylene bromide in Table IV. For methylene iodide, the distance between the carbon and iodine nuclei is taken as the sum of the atomic radii, 1.96 Å., and the calculation carried out as before. The angle between the doublet axes is found to be 135° and the resultant moment, therefore, 0.78 times that of methyl iodide, or $0.78 \times 1.31 \times 10^{-18} = 1.02 \times 10^{-18}$, in excellent agreement with the value in Table IV.

In similar fashion the chloroform molecule may be resolved into three doublets with their axes in the imaginary lines joining the carbon nucleus to the three chlorine nuclei which lie at the apices of an equilateral triangle. If there were no compression of the spheres of repulsion used in the calculation for methylene chloride, the carbon–chlorine bonds would be stretched even if the tetrahedral structure were so distorted that the carbon and the three chlorine nuclei were in the same plane. It appears reasonable to suppose that the hypothetical atomic spheres are somewhat compressed, but it is evident that the distortion of the tetrahedral structure of the mole-

[10] Rankine and Smith, *Phil. Mag.*, **42**, 601 (1921).

cule is greater than in the case of the methylene compound, which should cause the decrease in moment below that calculated for the undistorted tetrahedral structure to be greater. The separation of the chlorine nuclei is still considerably greater than the atomic diameter estimated from x-ray data, so that there is no need to suppose that the electron shells are appreciably deformed. This is in harmony with the fact that the atomic refraction of chlorine shows no significant variation between molecules containing one, two, three and four chlorines attached to the same carbon,[11] which would certainly not be the case if the electron shells of the halogens suffered increasing deformation as the number of halogens attached to one carbon increased.

Calculation leads to similar conclusions for bromoform and iodoform, although the distortion of the tetrahedral structure in the bromoform molecule should be less than in the molecules of the other two substances. Table IV shows the much lower values for the trihalogenated molecules. The moment of bromoform differs from Morgan's unpublished value for methyl bromide, to which it should be equal if the tetrahedral structure were undistorted, by an amount smaller than the differences observed for the chlorine and iodine compounds, thereby conforming with the result of the calculation. As the inductive effect of a doublet in one part of the molecule upon the rest of the molecule has been disregarded in these calculations and in view of the speculative nature of the argument concerning the atomic dimensions and the possible errors in some of the experimental values of moments quoted, the excellence of the agreement between the observed and the calculated moments of the methylene compounds must be somewhat fortuitous. It is evident, however, that the theory of the distortion of the molecule by repulsion explains satisfactorily the moments of the halogenated methanes.

Summary

The dielectric constants and densities of several alkyl halides and halogenated methanes in heptane or benzene have been determined over a wide range of temperature, and the data have been used to calculate the polarizations of the substances and the electric moments of their molecules.

The polarizations show that the orientation or association of the polar molecules depends upon the size of the electric moments of the molecules and the screening of their doublets by the molecular structure.

In the alkyl halides no measurable increase of electric moment accompanies increase of the number of carbon atoms beyond two.

In the di- and tri-halogenated methanes, repulsive forces between the halogens distort the structures and reduce the moments of the molecules.

[11] *Cf.* Smyth, *Phil. Mag.*, **50**, 361 (1925).

THE DIELECTRIC POLARIZATION OF LIQUIDS. II. ACETIC AND BUTYRIC ACIDS

The fatty acids have been so extensively investigated from many points of view that their dielectric behavior should be of unusual interest. Solutions of acetic acid in benzene and in ether were studied some years ago by Dr. S. O. Morgan and Dr. C. P. Smyth but, as the results were peculiar and as some doubt arose as to the purity of the acetic acid which had been employed, no use was made of the data. The measurements have been repeated with carefully purified acetic acid over a wider range of temperature and extended to butyric acid. The apparatus, with which the dielectric constant was determined at a wave length of 600 meters, has been described previously.[1]

Preparation of Materials

Benzene.—Benzene was purified in the usual manner, being finally dried and distilled over sodium; b. p. 80.1°; n_D^{20} 1.50135.

Ether.—U. S. P. ether was shaken several times with a strong sodium chloride solution containing a little sodium hydroxide, washed with water, dried over calcium chloride and distilled; b. p. 35.1°; d_4^{20} 0.7137.

Acetic Acid.—Merck's C. P. glacial acetic acid was crystallized twelve times, the final melting point being 16.6° and the refractive index n_D^{20} 1.37175. This sample was fractionally distilled; b. p. 117.8°; d_4^{20} 1.0491; n_D^{20} 1.37175.

Butyric Acid.—*n*-Butyric acid obtained from the Eastman Kodak Company was fractionally distilled, the fraction boiling between 163.2 and 163.4° being taken for the measurements; d_4^{20} 0.9591.

Experimental Results

For the acetic acid solutions and the pure substance the dielectric constants ϵ were measured at temperature intervals of approximately 10° and the densities d at intervals of about 15°. The values given for them in Table I were obtained by graphical interpolation. The butyric acid measurements were made at three fixed temperatures, which make interpolation unnecessary. The polarizations, P_2, of the acids were calculated by means of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{c_1 M_1 + c_2 M_2}{d} \text{ and } P_2 = \frac{P_{12} - P_1}{c_2} + P_1$$

in which P_{12} is the polarization of the mixture, and c_1 and c_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights, and polarizations of the individual components.

In the case of pure acetic acid slightly supercooled to 16.4°, a resistance

[1] Smyth, Morgan and Boyce, *J. Am. Chem. Soc.*, **50**, 1536 (1928); Smyth and Morgan, *ibid.*, **50**, 1547 (1928).

Table I

Dielectric Constants and Densities of Solutions and Polarizations of Acids

Benzene–Acetic Acid

Mole fr. CH_3COOH =	0	0.0978	0.2305	0.4372	0.6134	0.7912	1.000
t, °C.	ϵ						
0	2.336	2.375	2.464	2.706	3.113	3.956	
10	2.315	2.358	2.449	2.700	3.118	3.981	6.074
20	2.295	2.340	2.434	2.693	3.124	4.007	6.13
30	2.274	2.322	2.418	2.687	3.130	4.032	6.20
40	2.253	2.303	2.403	2.679	3.133	4.052	6.27
50	2.232	2.285	2.388	2.672	3.132	4.067	6.36
60	2.210	2.266	2.372	2.663	3.129	4.078	6.47
70	2.188	2.246	2.357	2.655	3.126	4.084	6.60
	d						
0	0.8986	0.9100	0.9222	0.9484	0.9760	1.0134	
10	.8896	.8989	.9113	.9369	.9645	1.0020	1.0607
20	.8786	.8879	.9006	.9257	.9532	0.9904	1.0491
30	.8682	.8768	.8901	.9144	.9418	.9788	1.0376
40	.8574	.8657	.8796	.9032	.9307	.9675	1.0264
50	.8466	.8546	.8688	.8920	.9193	.9562	1.0153
60	.8357	.8436	.8582	.8810	.9078	.9448	1.0039
70	.8246	.8327	.8475	.8698	.8964	.9333	0.9923
	P_∞	P_2					
0	21.3	22.6	24.7	26.9	29.4	32.4	
10	22.4	23.8	25.3	27.5	30.0	33.1	35.6
20	22.8	24.2	25.7	28.1	30.6	33.7	35.9
30	23.1	24.5	26.2	28.7	31.3	34.3	36.7
40	23.7	25.5	26.6	29.2	31.9	35.0	37.3
50	24.2	26.1	27.2	29.8	32.5	35.5	37.9
60	24.8	26.8	27.6	30.4	33.0	36.1	38.6
70	25.5	27.7	28.2	31.0	33.6	36.7	39.4

Ether–Acetic Acid

	0	0.0339	0.0673	0.1039	0.1269	0.3549	0.5233	0.7198	1.000
	ϵ								
0	4.746	4.817	4.869	4.966	5.015	5.489	5.793	6.28	
10	4.499	4.608	4.671	4.749	4.797	5.275	5.606	6.12	6.07
20	4.296	4.402	4.462	4.542	4.593	5.072	5.428	5.97	6.13
30	4.113	4.197	4.276	4.348	4.406	4.880	5.268	5.81	6.20
	d								
0	0.7370	0.7364	0.7532	0.7619	0.7669	0.8259	0.8731	0.9450	
10	.7254	.7276	.7414	.7504	.7556	.8146	.8628	.9342	1.0607
20	.7137	.7189	.7295	.7387	.7442	.8032	.8526	.9234	1.0491
30	.7021	.7102	.7176	.7271	.7328	.7918	.8424	.9126	1.0376
	P_∞	P_2							
0	64.0	57.3	57.3	45.6	44.9	41.0	39.5	38.6	
10	62.7	55.7	55.0	43.2	43.0	40.5	39.3	38.6	35.6
20	61.7	54.5	55.2	43.6	43.3	40.8	39.7	38.2	35.9
30	59.7	52.3	52.8	40.6	41.3	40.4	39.6	38.9	36.7

TABLE I (*Concluded*)

Benzene–Butyric Acid

Mole fr. C_3H_7COOH = 0	0.0379	0.0640	0.0894	0.1875	0.4729	0.7183	1.000
t, °C.				ϵ			
10	2.315	2.301	2.333	2.342	2.388	2.542	2.705	2.932
40	2.253	2.266	2.280	2.290	2.340	2.519	2.715	3.001
70	2.188	2.203	2.219	2.231	2.291	2.500	2.725	3.074
				d			
10	0.8896	0.8916	0.8933	0.8939	0.9026	0.9254	0.9435	0.9703
40	.8574	.8595	.8616	.8636	.8713	.8933	.9160	.9389
70	.8246	.8270	.8292	.8313	.8388	.8634	.8854	.9119
	P_∞				P_2			
10	31.4	31.2	32.4	33.0	33.5	34.7	34.6	35.6
40	33.1	33.7	34.5	34.3	34.8	36.3	36.6	37.5
70	33.9	34.5	35.8	35.6	36.6	37.9	38.4	39.5

of 3.6 ohms had to be inserted in series with the condenser in the opposite arm of the bridge to balance the small conductance of the liquid. At 85.1° the dielectric constant was 7.11 and the compensating resistance 41.5 ohms, and at 100.0° ϵ was 8.05 and the resistance 60.0 ohms. For the benzene solution containing a mole fraction 0.7912 of acetic acid, the resistance required at room temperature was negligible, but rose to 6.6 ohms at 90.6°. In the less concentrated solutions the conductance was negligibly small. In the ether solutions the conductances were small, as the temperature of measurement was not above 30°, but were detectable at concentrations of acid down to mole fraction 0.3549.

Discussion of Results

The acetic acid data in Table I do not agree precisely with the earlier unpublished values, but the small differences observed are no greater than might be expected in view of the difference in the material used and are insufficient to affect the conclusions to be drawn. When these earlier measurements were made upon acetic acid, the increase in the dielectric constant of the pure liquid with rising temperature was thought to be the first observed case of such a phenomenon, although it was known that the polarization of pure ethyl bromide increased with rising temperature. Since these first measurements were made, similar behavior has been observed for a number of secondary and tertiary octyl alcohols.[2] As the dielectric constants of the dilute benzene solutions decrease in the normal manner with rising temperature, there is an intermediate region of concentration within which the temperature coefficient of the dielectric constant is very small. Thus, the solution containing 0.6134 mole fraction of acetic acid shows a slight increase in ϵ with rising temperature up to 40° followed by an even more gradual decrease. The values of P_{12} which

[2] Smyth and Stoops, *J. Am. Chem. Soc.*, **51**, 3330 (1929).

are not shown in Table I increase with temperature throughout the entire range of concentration, although the increase is very slight in the dilute solutions where the effect of the almost constant polarization, P_1, of the benzene predominates. As the polarization P_2 of the acetic acid in the dilute solutions is lower than that of benzene, the P_{12}–c_2 curves pass through a flat minimum in a region where there is little change of P_{12} with concentration.

The reason for this peculiar behavior is to be sought in the strong molecular association which is known to occur in acetic acid. Freezing point and partition coefficient measurements show that the apparent molecular weight of acetic acid in dilute solution in benzene is close to 120, the weight which it would have if polymerized into double molecules.[3] X-ray investigations indicate that the molecules of the higher fatty acids in the solid state are paired[4] end to end with their carboxyl groups in contact and a similar conclusion has recently been drawn for the liquid.[5] Such a pairing should bring the electric moments of the single molecules into opposition with resultant partial or complete cancellation of one another's effects. It is easy to picture the acetic acid in dilute solution in benzene as consisting largely of these double molecules possessing little or no electric moment. The concentration of single molecules is so low in the solutions here measured that extrapolation of the P_2 values to $c_2 = 0$ gives not the polarization of the molecules existing singly but rather their polarization when paired in the double molecules. Since these values of P_∞ increase with rising temperature, presumably because of increasing dissociation into single molecules, it is evident that they are not wholly free from the effect of the small number of single molecules present. It may be concluded, however, that the polarization of the molecules in this complex state is not far from 20. The molar refraction of acetic acid for the sodium D line is 13.0.[6] The difference between this and 20 is little, if any, larger than the value which the atomic polarization P_A might be expected to have. Consequently, the dipole contribution to the polarization, P_M, must be close to zero, if not actually zero, the electric moments of the single acetic acid molecules being practically canceled in the complex molecules. This conclusion is in agreement with results privately communicated some years ago by Dr. L. Ebert, who obtained 18.85 as the value of P_∞ for acetic acid in benzene and 19.4 for the molar polarization of the solid measured at 0° with a wave length of 5 meters. As there is no dipole contribution to the polarization of the solid measured under

[3] Beckmann, *Z. physik. Chem.*, **22,** 610 (1897); Herz and Fischer, *Ber.*, **38,** 1138 (1905); Trautz and Moschel, *Z. anorg. allgem. Chem.*, **155,** 13 (1926).

[4] Müller, *J. Chem. Soc.*, **123,** 2043 (1923); Müller and Shearer, *ibid.*, **123,** 3156 (1923); Trillat, *Ann. phys.*, **6,** 5 (1926).

[5] Morrow, *Phys. Rev.*, **31,** 10 (1928).

[6] Landolt–Börnstein–Roth, "Tabellen," 5th ed.

these conditions, it is evident that P_∞ is made up of the electronic and atomic polarizations only, that is, $P_\infty = P_E + P_A$ and $P_M = 0$, which is equivalent to saying that the molecular complexes in the dilute benzene solutions possess no electric moment.

Apparently, when the concentration increases, these complexes, in spite of their lack of electric moment, affect one another sufficiently to cause increase of polarization. It seems possible that the higher dielectric constants of the more concentrated solutions may further the dissociation of the complexes into single molecules and so increase the polarization. The fact that the polarization increases with rising temperature would seem to support the attribution of the increase to the separation of single molecules rather than to the formation of a different type of complex. The absence of electric moment in the complexes in the dilute solutions and the closeness of the apparent molecular weight to that of a double molecule point to a polymerization to double molecules in which the carboxyl groups are in contact as indicated by the x-ray results. However, the mere assumption of the existence of single and double molecules without effect upon one another is inadequate to explain the observed phenomena. The freezing point measurements of Trautz and Moschel[3] give an apparent molecular weight of 117.5 for acetic acid when the mole fraction in the benzene solution is 0.0288, increasing to 124.9 when the mole fraction is 0.0650. This and similar results may indicate the formation of definite complexes containing more than two molecules, but it appears possible to explain the observed phenomena in terms of single and double molecules and strong intermolecular forces.

In the hope of reducing the intermolecular forces and the extent of the association, a solvent of higher dielectric constant than benzene was sought. Ether was adopted as being the only liquid of higher constant which, when dissolved in non-polar solvents, showed a polarization independent of concentration. Unfortunately, however, ether may form an addition compound with acetic acid and thus complicate the situation. The polarization of the acetic acid, P_2, calculated on the assumption that the polarization of the ether, P_1, is unaffected by the presence of the acid, shows a normal behavior, although the values for the dilute solutions contain errors larger than usual because of loss of ether by volatilization. The P_{12}–c_2 curve passes through a flat maximum in the region of high dilution where the apparent polarization of the acetic acid is higher than that of the ether. The value of P_M is calculated by subtracting from P_∞ the approximate value 20 found for $P_E + P_A$ and, from P_M, the electric moment 1.40×10^{-18} is obtained for the single acetic acid molecule. This value cannot be regarded as certain since it may be really the moment of an addition compound of acetic acid and ether, but there is some evidence in its favor.

In order to investigate the question of a definite equilibrium between single and double acetic acid molecules in ether solution, Mr. C. H. Lindsley has measured the distribution of acetic acid between water and ether at 25° over a range of concentration of 0.086 to 1.644 moles of acetic acid per liter of ether, a range within which lie the four most dilute solutions in Table I. The most constant value of the distribution coefficient was obtained when an equilibrium between single and double molecules was assumed. If a is the total number of moles per liter of acetic acid, all the acid being calculated as having molecular weight 60.04, and x is the concentration of single molecules, the equilibrium constant $K = x^2/(a - x)$. The mean value obtained for K was 2.7.

Since it has been shown that the double molecules have practically no moment and do not, therefore, contribute to the orientation polarization P_M and, since it has been assumed that the P_∞ obtained from the ether solutions is the polarization of the single molecules, the value of P_M observed at any concentration should be the orientation polarization for the single molecules $P_{M\infty}$ multiplied by the fraction of the acetic acid which is present as single molecules, that is, $P_M = (x/a)P_{M\infty}$. The values of P have been obtained by interpolation at 25° and those of P_M by subtracting from them $P_E + P_A = 20$. From the value $P_{M\infty} = 41$ thus obtained, the values of P_M have been calculated by means of K and the values of a and x calculated from it. The difference between the observed and calculated values of P_M is large at $c_2 = 0.1039$ and $c_2 = 0.1269$, but for the other solutions and the pure acid the average difference is only 1.9.

Since the value of K determined in the distribution measurements may be affected by the water with which the ether layer is saturated and since it may be different in the concentrated solutions and the pure acid from what it is in the dilute solutions, too much significance should not be attached to the agreement between the observed and calculated values of P_M. It may be said, however, that the entire behavior of acetic acid which has been described is consistent with the theory of its existence in single and double molecules, the force fields of which may affect one another and cause further abnormalities. As the moment of acetic acid might be expected to be not very different from that of methyl acetate, for which Williams[7] has found a value of 1.67×10^{-18}, the value 1.4×10^{-18} seems reasonable, but it must be borne in mind that there is a possibility that this is really the moment of an addition compound of acetic acid and ether.

The behavior of butyric acid is very similar to that of acetic. The dielectric constants of the pure liquid and the most concentrated solution increase with rising temperature. The dielectric constant is lowered

[7] Williams, *Physik. Z.*, **29**, 174 (1928).

by the lengthened hydrocarbon chain, which reduces the number of dipoles in unit volume so that pure butyric acid behaves much like a benzene solution containing 0.6 to 0.7 mole fraction of acetic acid. The two methylene groups which differentiate butyric from acetic acid have a combined refraction for the sodium D line of 9.2, which is their contribution to P_E for the compound. This is very nearly the difference between the values of P_∞ for the two substances. The larger proportion of hydrocarbon in the butyric acid molecule lessens the rate of increase of the polarization with decrease in the concentration of benzene in the mixture so that pure butyric acid happens to have the same polarization as acetic.

The close resemblance of butyric acid to acetic is what would be expected from freezing point and partition coefficient measurements and the indication of double molecules by x-ray studies. The single butyric acid molecules must have approximately the same moment as those of acetic acid and form similar complexes in which the carboxyl groups are in contact with one another, canceling their moments.[8]

Summary

The dielectric constants and densities of solutions of acetic and butyric acids have been measured at different temperatures, and the data have been used to calculate the polarizations of the substances.

The dielectric constants of the pure acids behave abnormally in that they increase with rising temperature instead of decreasing.

The results are shown to be consistent with the theory of the existence of the acids in single and double molecules, the latter of which have little or no electric moment. It must be supposed, however, that the molecular force fields may affect one another and cause further abnormalities.

[8] Since the submission of the manuscript of this paper for publication, Dr. C. T. Zahn has communicated to the authors a value 1.4×10^{-18} for the moment of acetic acid measured as vapor at high temperatures and low pressures where it must have existed as single molecules. This may be regarded as excellent confirmation of the value for what was thought to be the single acetic acid molecule in ether solution. Wolf, in a paper just published [*Physik. Z.*, **31**, 227 (1930)], obtains a value of 0.74×10^{-18} for acetic acid from measurements in benzene solution at 22°, a value of 0.68×10^{-18} for butyric acid and 0.63×10^{-18} for both propionic and isovaleric acid. In calculating these results he used an estimated value of P_A equal to 15% of the molar refraction, which the evidence cited above shows to be much too small in the case of acetic acid. If $P - P_E$ in our results is used to calculate the moments of acetic and butyric acid, the values obtained are close to those calculated by Wolf. As it has been shown that $P - P_E$ consists mainly of the atomic polarization P_A for molecular complexes, the values calculated for moments from these differences and attributed to single molecules would seem to have little significance. These results also cast doubt upon the moment assigned to the carboxyl group in aromatic compounds from measurements upon the strongly associated benzoic acid in benzene solution [Williams, *Chem. Rev.*, **6**, 589 (1929)].